Remarks/Arguments

I. **Applicants responds to Examiner's 35 U.S.C. § 103(a) rejections of Claims 36-68, 88-93, and 130 by amendment and traversal**

In paragraphs 2-4, the Examiner has stated that Claims 36-68, 88-93, and 130 stand rejected under 35 U.S.C. § 103(a) as being unpatentable over Ruoff, *et al.* (U.S. Patent 5,547,748) (hereinafter "*Ruoff*"). Applicants respectfully traverse the rejections.

Applicants invention is directed towards products by process and compositions in which single-walled carbon nanotubes are derivized by diazonium specie though reaction with the nanotube's side wall as demonstrated by the independent claims of the Application.

Claim 36, as amended, reads as follows:

36. A product made by the process comprising:
    (a)   selecting a plurality of carbon nanotubes; and
    (b)   reacting the plurality of carbon nanotubes with a diazonium specie to form derivatized carbon nanotubes, wherein a derivation occurs along the sidewalls of the carbon nanotube.

Claim 38, as amended, reads as follows:

38. A product made by the process comprising:
    (a)   selecting an assembly of single-wall carbon nanotubes;
    (b)   immersing the assembly in a solution comprising a diazonium specie; and
    (c)   applying a potential to the assembly to electrochemically react the assembly with the diazonium specie, wherein a reaction occurs along the sidewalls of the single-wall carbon nanotubes.

Claim 68, as amended, reads as follows:

68. A solution of single-wall carbon nanotubes made by the process of:

(a) a plurality of derivatized single-wall carbon nanotubes, wherein the plurality of derivatized carbon nanotubes were derivatized utilizing a diazonium specie and a derivation occurs along the sidewall of the carbon nanotube; and

(b) a solvent, wherein the derivatized plurality of carbon nanotubes are dispersed in the solvent.

Claim 88, as amended, reads as follows:

88. A product made by the process comprising:

    (a) preparing an assembly, wherein

        (i) the assembly comprises a first plurality of carbon nanotubes and a second plurality of carbon nanotubes; and

        (ii) wherein the carbon nanotubes in the first plurality and the carbon nanotubes in the second plurality can be individually addressed electronically;

    (b) immersing the assembly in a diazonium specie; and

    (c) applying a negative potential to the assembly to cause the first plurality to essentially come in contact with the second plurality; and

    (d) electrochemically reacting the assembly with the diazonium specie so as to foster a side-wall reaction for the plurality of carbon nanotubes.

Claim 89, as amended, reads as follows:

89. A product made by the process comprising:

    (a) preparing an assembly of carbon nanotubes

    (b) immersing the assembly in a first diazonium specie;

    (c) applying a potential to the assembly in a first direction;

    (d) electrochemically reacting the assembly with the first diazonium specie so as to foster a side-wall reaction with the assembly;

    (e) immersing the assembly in a second diazonium specie;

    (f) applying a potential to the assembly in a second direction; and

    (g) electrochemically reacting the assembly with the second diazonium specie.

Claim 130, as amended, reads as follows:

130. A product made by the process comprising:

(a) selecting a plurality of single-wall carbon nanotubes; and

(b) reacting the plurality of carbon nanotubes with a diazonium specie to form derivatized carbon nanotubes with derivations along the sidewall of the nanotube.

Regarding rejections under 35 U.S.C. § 103(a), to establish a *prima facie* case of obviousness, three basic criteria must be met. First, there must be some suggestion or motivation, either in the references themselves or in the knowledge generally available to one of ordinary skill in the art, to modify the reference or to combine reference teachings. Second, there must be a reasonable expectation of success. Finally, the prior art reference (or references when combined) must teach or suggest all the claim limitations. The teaching or suggestion to make the claimed combination and the reasonable expectation of success must both be found in the prior art and not based on applicant's disclosure. *See* M.P.E.P. § 706.02(j); *see also In re Vaeck*, 947 F.2d 488, 20 U.S.P.Q.2d 1438 (Fed. Cir. 1991).

A. The *Ruoff* reference, singly or in combination, does not sufficiently suggest or motivate, either by the reference itself or through knowledge generally available in the art, one of ordinary skill in the art to modify *Ruoff* to create Applicants' inventions.

Applicants respectfully point out that the motivation to modify *Ruoff* must come from one of three possible sources: the nature of the problem to be solved, the teachings of the prior art, and the knowledge of persons of ordinary skill in the art. *In re Rouffet*, 149 F.3d 1350, 1357, 47 U.S.P.Q.2d 1453, 1457-58 (Fed. Cir. 1998).

Applicants respectfully submit that the Examiner has not provided the source a person of ordinary skill in the art would derive motivation from with access to *Ruoff* to modify *Ruoff*'s teachings and suggestions from its current claimed form into products by process and compositions wherein the single walled carbon nanotubes are derivized by diazonium groups and derivation occurs *along the sidewalls* of the carbon nanotube.

The reference cited by the Examiner is inadequate for an obviousness rejection. *Ruoff* discusses functionalization at "strained corners", or corners where pentagonal and hexagonal links segments of a fullerene shape are interlinked together to create "sharp bends" in polyhedral geometries. *Ruoff* specifically emphasizes the importance of the pentagon segments and molecular strain at ridges and corners in permitting functionalization of the claimed nanopolyhedras *at those sites*:

> *An important feature of the faceted nanopolyhedra and nanoencapsulates are the sharp bends of the hexagonal lattice required between the polyhedral geometries*. In the pentahedron case, $\pi/2$ bends are required at the edges of the rectangular faces. *These sharp bends introduce strain energy* which is inversely proportional to the square of the radius of curvature. The bending radius in this case appears to be on the order of 2-3 ring diameters. *The strain at the bends, or corners, results in these areas being more reactive than the flat sides of the pentahedron.*
>
> . . .
>
> *The presence of pentagons is the key to the reactivity of simple fullerenes such as C^{60} and C^{70} (Taylor, 1991, 1992b). The pentagons introduce strain in the system and makes possible a variety of nucleophilic, radical, and electrophilic addition reactions. As mentioned above, an important feature of the carbon nanoencapsulates is the sharp corners, which are likely to be reactive.*
>
> *Similarly, nanoencapsulates may be reactive at the strained corners . . . .*

Ruoff, col. 8, lns. 29-53 (emphasis added); *see also* Fig. 5 (model of a pentahedral nanopolyhedron showing pentagonal and hexagonal links at edges).

Ruoff does not motivate one skilled in the art to modify *Ruoff* to create carbon nanotubes derivatized with a diazonium specie where derivation does occur along the *sidewall* of the fullerene nanotube. Firstly, *Ruoff* emphasizes the importance of reaction and derivation at "strained" or "sharp" sites; however, it is known to one of ordinary skill in the art that single-walled carbon nanotube sidewalls do not have "sharp bends" or "strained corners" along the tube's shaft (the nanotube's sidewall) that create physical strain and, therefore, makes derivation easier. Secondly, carbon nanotube sidewalls do not contain pentagon segments in their structure as *Ruoff*'s nanopolyhedria structures. *See* Carbon Nanotube, *available at*

http://en.wikipedia.org/wiki/Carbon_nanotube (printed February 15, 2007), attached hereto. Any such deviation, such as the inclusion of a pentagon segment in the sidewall of the carbon nanotube, would cause a fundamental change in the both tube's shape and thermal/chemical/other properties, potentially rendering it unsuitable for its intended purpose. *See* Carbon Nanotube, Defects, *available at* http://en.wikipedia.org/wiki/Carbon_nanotube#Defects (tensile, electrical, and thermal properties potentially altered); Graphene, Description, *available at* http://en.wikipedia.org/wiki/Graphene (printed Feb. 15, 2007), attached hereto, which dicusses warping of graphene sheets from 2D plane by inclusion of defect links such as pentane and heptane segments in the hexagon plane. Because the sidewalls of carbon nanotubes lack these "bends" and "corners" as well as "curved surfaces having pentagons", *Ruoff* simply does not lead one to the method for successfully derivatizing the sidewall of a carbon nanotube as claimed in this Application. Therefore, Examiner's statement that "treating a SWNT is obvious" to form any invention, in light of the teachings and suggestions of *Ruoff*, is in error.

In addition to the previous argument, Examiner's statement that "[t]he location of functionalization is deemed possessed or an obvious expedient" does not hold for any of the amended independent claims and Claim 130 - the claim in which this statement was directed. Applicants take exception to this leap in opinion to deem this "possessed or an obvious expedient" and respectfully traverse. Applicant respectfully points out that the Examiner's own subjective opinion is insufficient to support a *prima facie* case of obviousness. *In re Lee*, 61 U.S.P.Q.2d 1430, 1434 (Fed. Cir. 2002). Applicant asserts that the carbon nanotube sidewalls are chemically different than the endcaps and that, therefore, location of the claimed functionalization is important to the invention. The Examiner cannot show that the reactivity of the carbon nanotube sidewalls is the same as reaction along the end caps or loose edges of a carbon nanotube, and "deeming" it as so is improper.

The "tube" structure of a carbon nanotube is known to one of ordinary skill in the art to be made of repeating, interlocking hexagonal segments to form the tubular structure. The pattern, as previously stated, is akin to a graphene sheet. *See* Graphene, Description, *available at*

http://en.wikipedia.org/wiki/Graphene (printed February 15, 2007), attached hereto. It is also well known the art and has been previously argued that this tubular graphene structure is much more difficult to directly derivatize relative to the fullerene end-caps shapes at the ends of the carbon nanotubes, which contain bond strains. *See, generally,* Application, Background of Invention 2 ¶ [0005-6]. In fact, the end caps and the tube wall portions of the carbon nanotubes are literally two different fullerene components with different reactivity, bond strains, and structures. *See* Aziz, Hamza, "Routes to Carbon Nanotube Solubilization and Applications", *available at* http://www.lib.duke.edu/chem/chem110/papers?Hamaza%20Aziz.htm (last viewed Feb. 6, 2006), attached hereto. See, in particular, the section "Origins of Nanotube Chemistry". Examiner's opinion that "the claim only requires minimal reaction at one site" attempts to side-step and minimize the difficulty and non-obviousness as revealed with the previous facts in creating single-walled carbon nanotubes *with sidewall derivations* with diazonium species. One skilled in the art simply cannot use *Ruoff* and knowledge in the art to accomplish the claimed derivations.

Given all the discussed facts and knowledge in the art, a person of ordinary skill would not be motivated or have received suggestion to take *Ruoff*'s teachings and transform it into Applicants' inventions.

B. **Applicant respectfully submits that the Examiner has not provided or shown where in the prior art the reasonable expectation of success is for modifying *Ruoff* to make Claims 36, 38, 68, 88, 89, and 130 obvious.**

The Applicants respectfully suggests that the Examiner has not provided citation or reference to any source in the prior art that would guide one of ordinary skill to have a reasonable expectation of success, given *Ruoff*, to create the inventions claimed in Claims 36, 38, 68, 88, 89, and 130. The Applicant respectfully points out that the Examiner must provide evidence from where a reasonable expectation of success would be derived from by one of ordinary skill in the art in modifying *Ruoff* to render Claims 36, 38, 68, 88, 89, and 130 obvious. M.P.E.P. § 2143. The Applicant suggests that since the Examiner has not provided where the reasonable expectation of success lies, the Examiner has not presented a *prima facie* case of obviousness in rejecting Claims 36, 38, 68, 88, 89, and 130.

C.   Applicant respectfully points out that *Ruoff* does not teach or suggest all the claim limitations of Claims 36, 38, 68, 88, 89, and 130.

Applicant respectfully suggests that neither the cited reference – *Ruoff* – or knowledge of one of ordinary skill in the art, either singularly or in combination, teaches or suggests all the elements for derivatizing the sidewall of a single carbon nanotube with a diazonium specie. Because the reference and knowledge of the art do not provide all the claim limitations of Applicants' inventions, Examiner has not established the case for *prima facie* obviousness for these claims. All claim limitations present must be taught or suggested by the prior art to establish obvioiusness. *In re Royka*, 490 F.2d 981, 180 U.S.P.Q. 580 (C.C.P.A. 1974).

D.   Final remarks on 35 U.S.C. § 103(a) rejections

Applicant respectfully submits that the Examiner has not met the burden of establishing a prima facie case for obviousness in rejecting Claims 36, 38, 68, 88, 89, and 130 because the cited art and knowledge of one of ordinary skill in the art does not provide sufficient motivation or suggestion, provide a reasonable expectation of success, and teach or suggest all the claim limitations of the claimed inventions. As such, Applicant respectfully asserts that Claims 36, 38, 68, 88, 89, and 130 are in a condition of allowance. In addition, Applicant respectfully asserts all claims which depend from Claims 36, 38, 68, 88, 89, and 130 also now in condition for allowance. If an independent claim is nonobvious under 35 U.S.C. § 103, then any claim depending therefrom is nonobvious. *In re Fine*, 837 F.2d 1071, 5 U.S.P.Q.2d 1596 (Fed. Cir. 1988).

Conclusion

No new matter has been added. Applicant respectfully submits that Claims 36-68, 88-93, and 130 as they now stand are patentably distinct over the art cited during the prosecution thereof.

With the addition of no new claims, no additional filing fees are due. However, Applicant respectfully requests a (1) One Month Extension of Time to File this Response. Enclosed with this report is Form PTO/SB/22 with instruction to charge Extension Fees in the amount of $60.00 to our deposit account. If additional fees are due and are not included, the Director is hereby authorized to charge any fees or credit any overpayment to Deposit Account Number 23-2426 of WINSTEAD SECHREST & MINICK P.C. (referencing matter 11321-P022WUD1).

If the Examiner has any questions or comments concerning this paper or the present application in general, the Examiner is invited to call the undersigned at 713-650-2780.
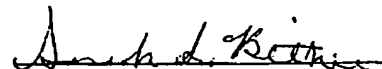
Respectfully submitted,

WINSTEAD SECHREST & MINICK P.C.

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CERTIFICATE OF MAILING UNDER 37 C.F.R. § 1.10

I hereby certify that the attached *Amendment and Response to Office Action* are being deposited with the USPS, with sufficient postage, as "Express Mail – Post Office to Addressee", mailing label number EL812637012US, addressed to Mail Stop Amendment, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on the date below:

_____2/16/07_____
Date

_____J. E. Olson_____
Signature

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11321-P022WUD1 2/15/2007

Carbon nanotube

From Wikipedia, the free encyclopedia

Carbon nanotubes (CNTs) are allotropes of carbon. A carbon nanotube is a one-atom thick sheet of graphite (called graphene) rolled up into a seamless cylinder with diameter of the order of a nanometer. This results in an essentially one-dimensional nanostructure where the length-to-diameter ratio exceeds 10,000. Such cylindrical carbon molecules have novel properties that make them potentially useful in a wide variety of applications in nanotechnology, electronics, optics and other fields of materials science. They exhibit extraordinary strength and unique electrical properties, and are efficient conductors of heat. Inorganic nanotubes have also been synthesized.

Nanotubes are members of the fullerene structural family, which also includes buckyballs. Whereas buckyballs are spherical in shape, a nanotube is cylindrical, with at least one end typically capped with a hemisphere of the buckyball structure. Their name is derived from their size, since the diameter of a nanotube is on the order of a few nanometers (approximately 50,000 times smaller than the width of a human hair), while they can be up to several millimeters in length. There are two main types of nanotubes: single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs).

The nature of the bonding of a nanotube is described by applied quantum chemistry, specifically, orbital hybridization. Nanotubes are composed entirely of sp^2 bonds, similar to those of graphite. This bonding structure, which is stronger than the sp^3 bonds found in diamond, provides the molecules with their unique strength. Nanotubes naturally align themselves into "ropes" held together by Van der Waals forces. Under high pressure, nanotubes can merge together, trading some sp^2 bonds for sp^3 bonds, giving great possibility for producing strong, unlimited-length wires through high-pressure nanotube linking.[1]
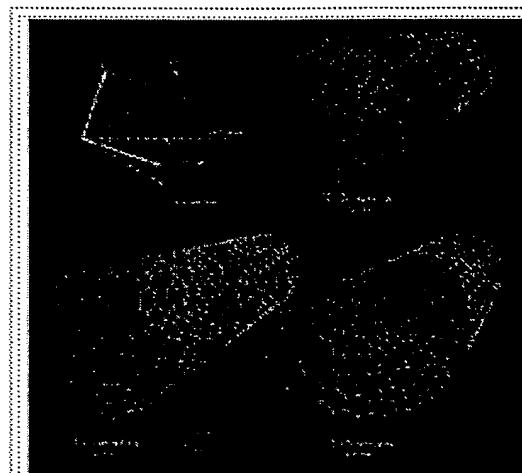
3D model of three types of single-walled carbon nanotubes.
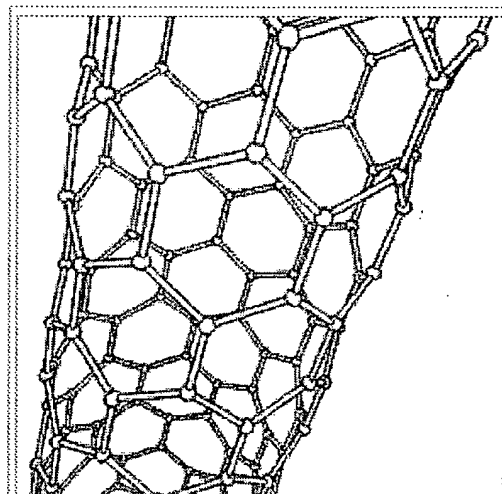
This animation of a rotating Carbon nanotube shows its 3D structure.

Contents

Discovery

See also: Timeline of carbon nanotubes

A 2006 editorial written by Marc Monthioux and Vladimir Kuznetsov in the journal *Carbon*[2] has described the interesting and often misstated origin of the carbon nanotube. A large percentage of academic and popular literature attributes the discovery of hollow, nanometer sized tubes composed of graphitic carbon to Sumio Iijima of NEC in 1991.

In 1952 Radushkevich and Lukyanovich published clear images of 50 nanometer diameter tubes made of carbon in the Russian *Journal of Physical Chemistry*[3]. This discovery was largely unnoticed, the article was published in the Russian language, and Western scientists' access to Russian press was limited during the Cold War. It is likely that carbon nanotubes were produced before this date, but the invention of the transmission electron microscope allowed the direct visualization of these structures.

Carbon nanotubes have been produced and observed under a variety of conditions prior to 1991. A paper by Oberlin, Endo, and Koyama published in 1976 clearly showed hollow carbon fibres with nanometer-scale diameters using a vapour-growth technique.[4] Additionally, the authors show a TEM image of a nanotube consisting of a single wall of graphene. Later, Endo has referred to this image as a single walled nanotube [5].

In 1981 a group of Ukrainian scientists published the results of chemical and structural characterization of carbon nanoparticles produced by a thermocatalytical disproportionation of carbon monoxide [6]. Using TEM images and XRD patterns, the authors suggested that their "Carbon multi-layer tubular crystals" were formed by rolling graphene layers into cylinders. Additionally, they speculated that during rolling graphene layers into a cylinder, many different arrangements of graphene hexagonal nets are possible. They suggested two possibilities of such arrangements: circular arrangement (armchair nanotube) and a spiral, helical arrangement (chiral tube).

In 1987, Howard G. Tennent of Hyperion Catalysis was issued a U.S. patent for the production of "cylindrical discrete carbon fibrils" with a "constant diameter between about 3.5 and about

70 nanometers..., length 10^2 times the diameter, and an outer region of multiple essentially continuous layers of ordered carbon atoms and a distinct inner core...."[7].

Iijima's discovery of carbon nanotubes in the insoluble material of arc-burned graphite rods[8] created the buzz that is now associated with carbon nanotubes. Nanotube research accelerated greatly following the independent discoveries[9][10] by Bethune at IBM[11] and Iijima at NEC of *single-wall* carbon nanotubes and methods to specifically produce them by adding transition-metal catalysts to the carbon in an arc discharge. The arc discharge technique was well-known to produce the famed Buckminster fullerene on a preparative scale,[12] and these results appeared to extend the run of accidental discoveries relating to fullerenes. The original observation of fullerenes in mass spectrometry was not anticipated, [13] and the first mass-production technique by Kratchmer and Huffman was used for several years before realising that it produced fullerenes.[14]

The discovery of nanotubes remains a contentious issue, especially because several scientists involved in early nanotube could be likely candidates for the Nobel Prize. Many believe that Iijima's report in 1991 is of particular importance because it brought carbon nanotubes into the awareness of the scientific community as a whole. A review of the history of the discovery of carbon nanotubes is presented in *Carbon 44, 1621, 2006.*

Types of carbon nanotubes

Single-walled

Most single-walled nanotubes (SWNT) have a diameter of close to 1 nanometer, with a tube length that can be many thousands of times longer. Single-walled nanotubes with length up to orders of centimeters have been produced [15]. The structure of a SWNT can be conceptualized by wrapping a one-atom-thick layer of graphite called graphene into a seamless cylinder. The way the graphene sheet is wrapped is represented by a pair of indices (n,m) called the chiral vector. The integers n and m denote the number of unit vectors along two directions in the honeycomb crystal lattice of graphene. If $m=0$, the nanotubes are called "zigzag". If $n=m$, the nanotubes are called "armchair". Otherwise, they are called "chiral".

The (n,m) nanotube naming scheme can be thought of as a vector (C_h) in an infinite graphene sheet that describes how to "roll up" the graphene sheet to make the nanotube. T denotes the tube axis, and a_1 and a_2 are the unit vectors of graphene in real space.

Single-walled nanotubes are a very important variety of carbon nanotube because they exhibit important electric properties that are not shared by the multi-walled carbon nanotube (MWNT) variants. Single-walled nanotubes are the most likely candidate for miniaturizing electronics past the micro electromechanical scale that is currently the basis of modern electronics. The most basic building block of these systems is the electric wire, and SWNTs can be excellent conductors[16]. One useful application of SWNTs is in the development of the
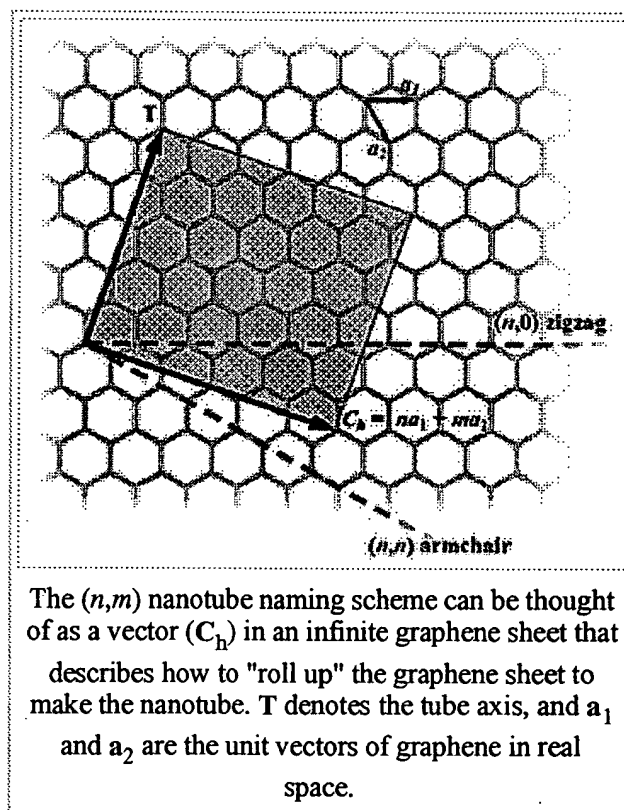
first intramolecular field effect transistors (FETs). The production of the first intramolecular logic gate using SWNT FETs has recently become possible as well[17]. To create a logic gate you must have both a p-FET and an n-FET. Because SWNTs are p-FETs when exposed to oxygen and n-FETs when unexposed to oxygen, they were able to protect half of a SWNT from oxygen exposure, while exposing the other half to oxygen. The result was a single SWNT that acted as a NOT logic gate with both p and n-type FETs within the same molecule.

Single-walled nanotubes are still very expensive to produce, and the development of more affordable synthesis techniques is vital to the future of carbon nanotechnology. If cheaper means of synthesis cannot be discovered, it would make it financially impossible to apply this technology to commercial-scale applications.[18]

Multi-walled

Multiwalled nanotubes (MWNT) consist of multiple layers of graphite rolled in on themselves to form a tube shape. There are two models which can be used to describe the structures of multiwalled nanotubes. In the *Russian Doll* model, sheets of graphite are arranged in concentric cylinders, eg a (0,8) single-walled nanotube (SWNT) within a larger (0,10) single-walled nanotube. In the *Parchment* model, a single sheet of graphite is rolled in around itself, resembling a scroll of parchment or a rolled up newspaper. The interlayer distance is close to the distance between graphene layers in graphite. The special place of Double-walled Carbon Nanotubes (DWNT) must be emphasized here because they combine very similar morphology and properties as compared to SWNT, while improving significantly their chemical resistance. This is especially important when functionalisation is required (this means grafting of chemical functions at the surface of the nanotubes) to add new properties to the CNT. In the case of SWNT, covalent functionalisation will break some C=C double bonds, leaving "holes" in the structure on the nanotube and thus modifying both its mechanical and electrical properties. In the case of DWNT, only the outer wall is modified. DWNT synthesis on the gram-scale was first proposed in 2003 [19] by the CCVD technique, from the selective reduction of oxides solid solutions in methane and hydrogen.

Fullerite

Fullerites are the solid-state manifestation of fullerenes and related compounds and materials. Being highly incompressible nanotube forms, polymerized single walled nanotubes (P-SWNT) are a class of fullerites and are comparable to diamond in terms of hardness. However, due to the way that nanotubes intertwine, P-SWNTs don't have the corresponding crystal lattice that makes it possible to cut diamonds neatly. This same structure results in a less brittle material, as any impact that the structure sustains is spread out throughout the material.

Torus

A nanotorus is a carbon nanotube bent into a torus (donut shape). Nanotori have many unique properties, such as magnetic moments 1000 times larger than previously expected for certain specific radii.[20] Many properties such as magnetic moment, thermal stability, etc. vary widely depending on radius of the torus and radius of the tube.[21]

Properties

Strength

Carbon nanotubes are one of the strongest and stiffest materials known, in terms of tensile strength and elastic modulus respectively. This strength results from the covalent sp^2 bonds formed between the individual carbon atoms. In 2000, a multi-walled carbon nanotube was tested to have a tensile strength of 63 GPa.[22] In comparison, high-carbon steel has a tensile strength of approximately 1.2 GPa. CNTs have very high elastic modulus, on the order of 1 TPa.[23] Since carbon nanotubes have a low density for a solid of 1.3-1.4 g/cm^3[24], its specific strength of up to 48,462 kN·m/kg is the best of known materials, compared to high-carbon steel's 154 kN·m/kg.

Under excessive tensile strain, the tubes will undergo plastic deformation, which means the deformation is permanent. This deformation begins at strains of approximately 5% [25] and can increase the maximum strain the tube undergoes before fracture by releasing strain energy.

CNTs are not nearly as strong under compression. Because of their hollow structure and high aspect ratio, they tend to undergo buckling when placed under compressive, torsional or bending stress.

Kinetic

Multiwalled carbon nanotubes, multiple concentric nanotubes precisely nested within one another, exhibit a striking telescoping property whereby an inner nanotube core may slide, almost without friction, within its outer nanotube shell thus creating an atomically perfect linear or rotational bearing. [26][27] This is one of the first true examples of molecular nanotechnology, the precise positioning of atoms to create useful machines. Already this property has been utilized to create the world's smallest rotational motor[28] and a nanorheostat.[29] Future applications such as a gigahertz mechanical oscillator are also envisaged.[30]

Electrical

> *See also: Fermi point*

Because of the symmetry and unique electronic structure of graphene, the structure of a nanotube strongly affects its electrical properties. For a given (n,m) nanotube, if $n + m = 3q$ (where q is an integer), then the nanotube is metallic, otherwise the nanotube is a semiconductor. Thus all armchair $(n=m)$ nanotubes are metallic, and nanotubes (5,0), (6,4), (9,1), etc. are semiconducting. In theory, metallic nanotubes can have an electrical current density more than 1,000 times greater than metals such as silver and copper[31].

Thermal

All nanotubes are expected to be very good thermal conductors along the tube, exhibiting a property known as "ballistic conduction," but good insulators laterally to the tube axis. It is predicted that carbon nanotubes will be able to transmit up to 6000 watts per meter per kelvin at room temperature; compare this to copper, a metal well-known for its good thermal conductivity, which only transmits 385 W/m/K. The temperature stability of carbon nanotubes is estimated to be up to 2800 degrees Celsius in vacuum and about 750 degrees Celsius in air.[32]

Defects

As with any material, the existence of defects affects the material properties. Defects can occur in the form of atomic vacancies. High levels of such defects can lower the tensile strength by up to 85%.[33] Another well-known form of defect that occurs in carbon nanotubes is known as the Stone Wales defect, which creates a pentagon and heptagon pair by rearrangement of the bonds. Because of the almost one-dimensional structure of CNTs, the tensile strength of the tube is dependent on the weakest segment of it in a similar manner to a chain, where a defect in a single link diminishes the strength of the entire chain.

The tube's electrical properties are also affected by the presence of defects. A common result is the lowered conductivity through the defective region of the tube. Some defect formation in armchair-type tubes (which are metallic) can cause the region surrounding that defect to become semiconducting. Furthermore single monoatomic vacancies induce magnetic properties.

The tube's thermal properties are heavily affected by defects. Such defects lead to phonon scattering, which in turn increases the relaxation rate of the phonons. This reduces the mean free path, and reduces the thermal conductivity of nanotube structures.

Synthesis

Techniques have been developed to produce nanotubes in sizeable quantities, including arc discharge, laser ablation, high pressure carbon monoxide (HiPco), and chemical vapor deposition (CVD). Most of these processes take place in vacuum or with process gases. CVD growth of CNTs can take place in vacuum or at atmospheric pressure. Large quantities of nanotubes can be synthesized by these methods; advances in catalysis and continuous growth processes are making CNTs more commercially viable.

It is now thought by some that the catalysts or methods involved in forging damascus steel (a forging technique lost to time) may provide vital hints for manufacturing nanotubes cheaply, after they were recently discovered to be a component of that ancient sword metal[34] [35].

Arc discharge

Nanotubes were observed in 1991 in the carbon soot of graphite electrodes during an arc discharge, by using a current of 100 amps, that was intended to produce fullerenes[36]. However the first macroscopic production of carbon nanotubes was made in 1992 by two researchers at NEC's Fundamental Research Laboratory. The method used was the same as in 1991. During this process, the carbon contained in the negative electrode sublimates because of the high temperatures caused by the discharge. Because nanotubes were initially discovered using this technique, it has been the most widely used method of nanotube synthesis.

The yield for this method is up to 30 percent by weight and it produces both single- and multiwall nanotubes, however they are quite short (50 microns).[37]

Laser ablation

In the laser ablation process, a pulsed laser vaporizes a graphite target in a high temperature reactor while an inert gas is bled into the chamber. The nanotubes develop on the cooler surfaces of the reactor,

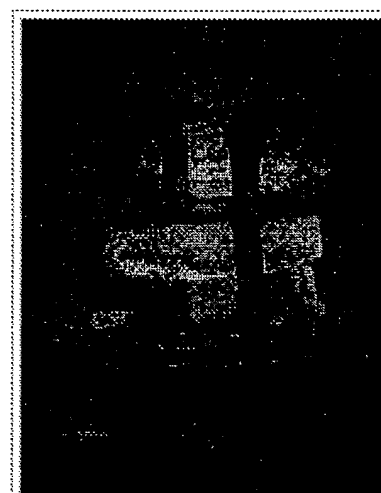as the vaporized carbon condenses. A water-cooled surface may be included in the system to collect the nanotubes.

It was invented by Richard Smalley and co-workers at Rice University, who at the time of the discovery of carbon nanotubes, were blasting metals with the laser to produce various metal molecules. When they heard of the discovery they substituted the metals with graphite to create multi-walled carbon nanotubes. [38]. Later that year the team used a composite of graphite and metal catalyst particles (the best yield was from a cobalt and nickel mixture) to synthesise single-walled carbon nanotubes.[39]

This method has a yield of around 70% and produces primarily single-walled carbon nanotubes with a controllable diameter determined by the reaction temperature. However, it is more expensive than either arc discharge or chemical vapor deposition.[40]

Chemical vapor deposition (CVD)

The catalytic vapor phase deposition of carbon was first reported in 1959,[41] but it was not until 1993[42] that carbon nanotubes could be formed by this process.

During CVD, a substrate is prepared with a layer of metal catalyst particles, most commonly nickel, cobalt, iron, or a combination. The metal nanoparticles can also be produced by other ways, including reduction of oxides or oxides solid solutions. The diameters of the nanotubes that are to be grown are related to the size of the metal particles. This can be controlled by patterned (or masked) deposition of the metal, annealing, or by plasma etching of a metal layer. The substrate is heated to approximately 700°C. To initiate the growth of nanotubes, two gases are bled into the reactor: a process gas (such as ammonia, nitrogen, hydrogen, etc.) and a carbon-containing gas (such as acetylene, ethylene, ethanol, methane, etc.). Nanotubes grow at the sites of the metal catalyst; the carbon-containing gas is broken apart at the surface of the catalyst particle, and the carbon is transported to the edges of the particle, where it forms the nanotubes. This mechanism is

Nanotubes being grown by plasma enhanced chemical vapor deposition

still under discussion. The catalyst particles can stay at the tips of the growing nanotube during the growth process, or remain at the nanotube base, depending on the adhesion between the catalyst particle and the substrate.

If a plasma is generated by the application of a strong electric field during the growth process (plasma enhanced chemical vapor deposition), then the nanotube growth will follow the direction of the electric field.[43] By properly adjusting the geometry of the reactor it is possible to synthesize vertically aligned carbon nanotubes (i.e., perpendicular to the substrate), a morphology that has been of interest to researchers interested in the electron emission from nanotubes. Without the plasma, the resulting nanotubes are often randomly oriented, resembling a bowl of spaghetti. Under certain reaction conditions, even in the absence of a plasma, closely spaced nanotubes will maintain a vertical growth direction resulting in a dense array of tubes resembling a carpet or forest.

Of the various means for nanotube synthesis, CVD shows the most promise for industrial scale deposition in terms of its price/unit ratio. There are additional advantages to the CVD synthesis of

nanotubes. Unlike the above methods, CVD is capable of growing nanotubes directly on a desired substrate, whereas the nanotubes must be collected in the other growth techniques. The growth sites are controllable by careful deposition of the catalyst. Additionally, no other growth methods have been developed to produce vertically aligned nanotubes.

Recently, this area of synthesis has been advanced by a team of researchers at Rice University. The team, until recently led by the late Dr. Richard Smalley, has concentrated upon finding methods to produce large, pure amounts of particular types of nanotubes. Their approach grows long fibers from many small seeds cut from a single nanotube; all of the resulting fibers were found to be of the same diameter as the original nanotube and are expected to be of the same type as the original nanotube. Further characterization of the resulting nanotubes and improvements in yield and length of grown tubes are needed.[44]

Natural, incidental, and controlled flame environments

Fullerenes and carbon nanotubes are not necessarily products of high-tech laboratories; they are commonly formed in such mundane places as ordinary flames,[45] produced by burning methane,[46] ethylene,[47] and benzene,[48] and they have been found in soot from both indoor and outdoor air.[49] However, these naturally occurring varieties can be highly irregular in size and quality because the environment in which they are produced is often highly uncontrolled. Thus, although they can be used in some applications, they can lack in the high degree of uniformity necessary to meet many needs of both research and industry. Recent efforts have focused on producing more uniform carbon nanotubes in controlled flame environments.[50][51][52][53]

Potential, Current and Ancient Applications

See also, for last current applications: Timeline of carbon nanotubes

The strength and flexibility of carbon nanotubes makes them of potential use in controlling other nanoscale structures, which suggests they will have an important role in nanotechnology engineering. The highest tensile strength an individual multi-walled carbon nanotube has been tested to be is 63 GPa.[54] Bulk nanotube materials may never achieve a tensile strength similar to that of individual tubes, but such composites may nevertheless yield strengths sufficient for many applications. Carbon nanotubes have already been used as composite fibers in polymers to improve the mechanical, thermal and electrical

The joining of two carbon nanotubes with different electrical properties to form a diode has been proposed.

properties of the bulk product. A 2006 study published in *Nature* determined that some carbon nanotubes are present in damascus steel, possibly helping to account for their legendary strength[55] [56].

Structural

Because of the great mechanical properties of the carbon nanotubule, a variety of structures has been proposed ranging from everyday items like clothes and sports gear to combat jackets and space elevators (The Space Elevator, by Brad C. Edwards, NASA). However, the space elevator will require further efforts in refining carbon nanotube technology, as the practical tensile strength of carbon nanotubes can still be greatly improved.[57]

For perspective, outstanding breakthroughs have already been made. Pioneering work lead by Ray H. Baughman at the NanoTech Institute has shown that single and multi-walled nanotubes can produce materials with toughness un-matched in the man-made and natural worlds.[58]

A good example of a practical use for the carbon nanotubules is the bicycle Floyd Landis used at the 2006 Tour de France, the SLC 01 from BMC, a Swiss bike manufacturer. Carbon nanotubes were used to enhance the strength of the carbon fiber frame and made it possible to make a bicycle's frame weighing only one kilogram.[59]

Recent research by James D. Iverson and Brad C. Edwards has revealed the possibility of cross-linking CNT molecules prior to incorporation in a polymer matrix to form a super high strength composite supermaterial. This CNT composite will have a tensile strength on the order of 20 million psi (138 GPa, for 106 MN·m/kg), revolutionizing many aspects of engineering design where low weight and high strength is required.

In electrical circuits

Carbon nanotubes have many properties—from their unique dimensions to an unusual current conduction mechanism—that make them ideal components of electrical circuits.

Nanotube based transistors have been made that operate at room temperature and that are capable of digital switching using a single electron. [60]

One major obstacle to realization of nanotubes has been the lack of technology for mass production. However, in 2001 IBM researchers demonstrated how nanotube transistors can be grown in bulk, not very different from silicon transistors. The process they used is called "constructive destruction" which includes the automatic destruction of defective nanotubes on the wafer.[61]

This has since then been developed further and single-chip wafers with over ten billion correctly aligned nanotube junctions have been created. In addition it has been demonstrated that incorrectly aligned nanotubes can be removed automatically using standard lithography equipment.[62]

The first nanotube made integrated memory circuit was made in 2004. One of the main challenges have been regulating the conductivity of nanotubes. Depending on subtle surface features a nanotube may act as a plain conductor or as a semiconductor. A fully automated method has however been developed to remove non-semiconductor tubes. [63]

Nanoelectromechanical Systems (NEMS)

Carbon nanotubes have also been implemented in nanoelectromechanical systems, including mechanical memory elements (NRAM being developed by Nantero Inc.) and nanoscale electric motors (see Nanomotor).

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Stephen Hawking

External links and sources

- New Scientist Special Report (http://www.newscientisttech.com/channel/tech/nanotechnology) - a collection of nanotechnology articles, most on nanotubes
- The stuff of dreams (http://news.com.com/The+stuff+of+dreams/2009-1008_3-5091267.html?tag=nl) - CNET
- The Nanotube site (http://www.pa.msu.edu/cmp/csc/NTSite/nanopage.html) - Last updated 2006.09.17
- Nanotechnologies and nanotubes (http://www.chimica.unipd.it/enzo.menna/pubblica/nanobookmark.html)

- Nanowerk - Information on carbon nanotubes (http://www.nanowerk.com/n_nanomaterials_7.html)
- Animation of a (29,0) being struck by 10 sets of 9 Argon atoms at 10 eV each (http://sinnott.mse.ufl.edu/Movies/29x0-swnt_deflex_Ar10eV.mpg) (opens in media player)
- The wonderous World of Carbon Nanotubes (http://students.chem.tue.nl/ifp03/Wondrous%20World%20of%20Carbon%20Nanotubes_Final.pdf) (In .pdf format, good introduction to nanotube)
- nanotechweb.org (http://nanotechweb.org/) nanotube and nanotechnology news and information
- Carbon - Super Stuff (http://www.forskning.no/Artikler/2006/juni/1149432180.36) Educational interactive with narration and 3D-models of nanotube, diamond, graphite and coal.
- Carbon nanotube on arxiv.org (http://xstructure.inr.ac.ru/x-bin/theme2.py?arxiv=cond-mat&level=2&index1=43)
- Untangling and Dispersing of Carbon Nanotubes using Ultrasonics (http://hielscher.com/ultrasonics/nano_03.htm)
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- Carbon nanotech may have given swords of Damascus their edge - Nature 2006 (http://www.nature.com/news/2006/061113/full/061113-11.html)

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Categories: Articles with unsourced statements since February 2007 | All articles with unsourced statements | Nanomaterials | Carbon forms

Graphene

From Wikipedia, the free encyclopedia.

Graphene is a single planar sheet of sp²-bonded carbon atoms. It is not an allotrope of carbon because the sheet is of finite thickness. Graphenes are the 2-D counterparts of 3-D graphite. They are aromatic.

Contents

- 1 Description
- 2 Chemical modification
- 3 References
- 4 See also
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Description

Perfect graphenes consist exclusively of hexagonal cells; pentagonal and heptagonal cells constitute defects. If an isolated pentagonal cell is present, then the plane warps into a cone shape; insertion of 12 pentagons would create a fullerene. Likewise, insertion of an isolated heptagon causes the sheet to become saddle-shaped. Controlled addition of pentagons and heptagons would allow a wide variety of shapes to be made.
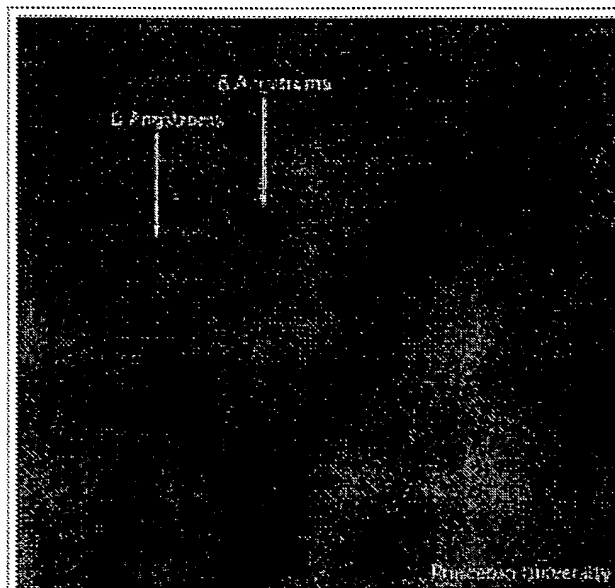

Figure 1. This image was captured using a Digital Multimode AFM (atomic force microscope). Notice the step from the substrate at zero height to a graphene flake about 8 angstroms high, which is on the order of a monolayer.

Carbon nanotubes may be considered to be graphene cylinders; some have a hemispherical graphene cap (that includes 6 pentagons) at each end. Graphenes have also attracted the interest of technologists who see them as a way of constructing ballistic transistors. In March 2006, Georgia Tech researchers announced that they had successfully built an all-graphene planar field-effect transistor and a quantum interference device. [1]

The IUPAC compendium of technology states: "previously, descriptions such as graphite layers, carbon layers, or carbon sheets have been used for the term graphene...it is not correct to use for a single layer a term which includes the term graphite, which would imply a three-dimensional structure. The term graphene should be used only when the reactions, structural relations or other properties of individual layers are discussed".

Writing in Science [2] , physicist Konstantin Novoselov and coworkers from the University of Manchester and the Institute of Microelectronics Technology and High Purity Materials at Chernogolovka state:

> Graphene is the name given to a single layer of carbon atoms densely packed into a benzene-ring structure, and is widely used to describe properties of many carbon-based materials, including graphite, large fullerenes, nanotubes, etc. (e.g., carbon nanotubes are usually thought of as

graphene sheets rolled up into nanometer-sized cylinders). Planar graphene itself has been presumed not to exist in the free state, being unstable with respect to the formation of curved structures such as soot, fullerenes, and nanotubes.

The researchers went on to construct graphenes by mechanical exfoliation (repeated peeling) of small "mesas" of highly oriented pyrolytic graphite; their motivation was to study the electrical properties of graphene. Mobilities of up to 10^4 cm²V^{-1}s^{-1} were reported; this value was almost independent of temperature. In addition, graphene has been shown to exhibit quantum Hall effect properties.

Similar work is ongoing at Princeton University in Professor Ali Yazdani's laboratory by three researchers: Dan Kuncik, Josh Moskowitz, and Patrick Ho. Many of the results obtained by the Novoselov group in their PNAS paper "Two-dimensional atomic crystals" [3] have been confirmed by the Yazdani group's work. For an example of a sample on the order of a monolayer, see figure 1.

Chemical modification

Soluble fragments of graphene can be prepared in the laboratory [4] through chemical modification of graphite. First, microcrystalline graphite is treated with a strongly acidic mixture of sulphuric acid and nitric acid. A series of steps involving oxidation and exfoliation result in small graphene plates with carboxyl groups at their edges. These are converted to acid chloride groups by treatment with thionyl chloride; next, they are converted to the corresponding graphene amide via treatment with octadecylamine. The resulting material (circular graphene layers of 5.3 angstrom thickness) is soluble in tetrahydrofuran, tetrachloromethane, and dichloroethane.

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See also

- Aromaticity
- Fullerenes
- Polycyclic aromatic hydrocarbons
- Carbon nanotubes

External links

- Image Gallery - Graphite and Graphene (http://www.ewels.info/img/science/)
- BBC News report (http://news.bbc.co.uk/2/hi/science/nature/3944651.stm)
- Electrons lose their mass in carbon sheets (http://physicsweb.org/articles/news/9/11/6/1) Physics Web (09-Nov-2005)
- In graphene, electron velocity is independent of energy. (http://www.zpenergy.com/modules.php?name=News&file=article&sid=1798)
- Potential for graphene computer chips, with explanation of technical issues/problems (http://gtresearchnews.gatech.edu/newsrelease/graphene.htm)
- Quantum weirdness on the end of your pencil (http://www.newscientist.com/channel/fundamentals/mg19125591.700) Philip Ball, New Scientist Magazine issue 2559, (8 July 2006)

- Links to external chemical sources

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Routes to Carbon Nanotube Solubilization and Applications

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Submitted November 25, 2003

ABSTRACT

This review covers development in nanotube functionalization from March 2002 to November 2003. Emphasis is given to organic, biological and device-oriented functionalization. In organic functionalization, mostly sidewall reactions are discussed because they form the majority of research corpus. The studies cited show that great strides have been made since last year in nanotube functionalization toward their use as devices in biological and electronic setting.

Outline

Introduction

When transition metal nanoparticles such as Ni/Co, Fe/Mo, Ni/Y, Rh/Pt are allowed to supersaturate with dissolved carbon, a cylindrical graphitic network forms giving rise to carbon nanotubes[1]. Depending on chirality and diameter, Single-Wall Carbon NanoTubes (SWNT)s have the

unique characteristic of being either metallic or semi-conducting. Their remarkable physical [1],

electronic,[2] and chemical[3] properties have opened the potential for their use in sundry applications

ranging from reinforced fibers and nanocomposites[4] to field-emission devices[5] to capability of

hydrogen storage[6].

However, many of these applications require modifications to the pristine nanotube to render it

functionally active for the various applications. The central problem in carbon nanotube

functionalization remains a method of modifying while preserving the strength and conductivity of

nanotubes. Many of the efforts so far in functionalization have been directed towards solubalization of

nanotubes and nanotube bundles[7]. Herein, we present a review of investigations from March 2002 to

November 2003 dealing with modifications and functionalization of carbon nanotubes that take

advantage of nanotube structure. Furthermore, a review of application in biological and electrical fields

of functionalized nanotubes is also presented.

Methods

I used Web of Science and Journal of American Chemical Society's webpage to find my

articles. I limited my search to articles from March 2002 to November 2003. From an external tip, I

also looked at the special edition of Accounts of Chemical Research on Carbon Nanotubes. The review

articles in this edition were extremely helpful in explaining the background to the current research.

Most of my searches were title searches with words "functionalized carbon nanotubes" or "nanotube

functionalization" etc. I often used the advance search feature to specify my search to specific time

period and journals.

Origins of Nanotube Chemistry

Most of the carbon nanotube chemistry arises from its inherent curvature. In fact, one can divide

a nanotube into different areas by curvature, which reveals that nanotubes are essentially a two-

component molecule with two terminal caps and a long, uniform cylinder. The caps resemble and

chemically behave like fullerenes. The caps are more reactive than the sidewalls and prone to oxidation

and addition reactions. Sidewalls are a little less strained and more inert.

The theoretical basis for this chemical non-equivalence is that curvature induces

pyramidalization (strain) and misalignment of π orbitals[3]. As Figure 1 shows, regular sp^2-hybridized

carbons have a 0° pyramidalization angle, θ_p, while regular sp^3-hybridized carbons have a θ_p of 19.47°. In for example the cap of a (5,5) carbon nanotube, sp^2 hybridized carbons have a pyramidalization angle of 11.6° (same as C_{60}) due to the curvature. In addition to strain from pyramidalization angle, nanotubes also have torsional strain from the C-C bonds that run diagonal to the circumference and thus have π orbital misalignment. In Figure 2, the bottom circle highlights one such bond with a misalignment angle Φ of 21.3°. Calculations show that in nanotubes, pi-orbital misalignment is most likely the major source of strain. Finally, the degree of pyramidalization and π orbital misaligment is inversely proportional to diameter, which suggests that smaller nanotubes are likely to be more reactive and SWNT more reactive than multi-wall nanotubes (MWNT) which have diamters in 20-50nm range.
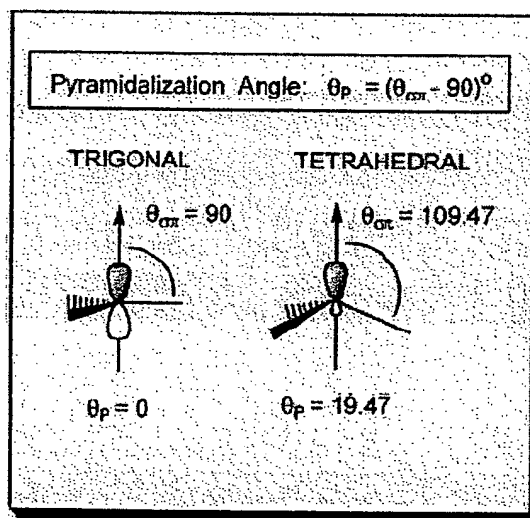

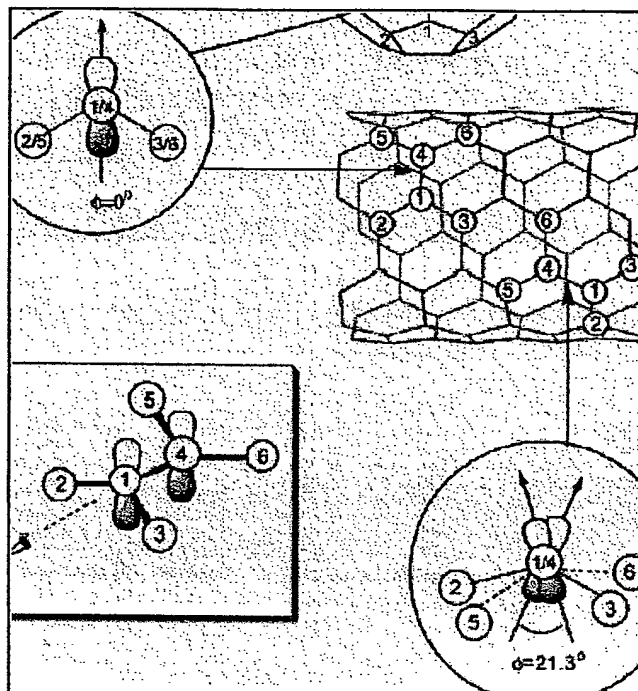Figure 0-1: Diagram of pyramidalization angle (θp). *Taken from Acc. Chem. Res. 35(12).*

Figure 2: Diagram of pi orbital misalignment. *Taken from Acc. Chem. Res. 35(12).*

Organic Functionalization

- **Fluorination**

Fluorination is a common pathway to a lot derivatization reactions [8] ranging from organolithums to alkoxides to amines. Although fluorination is a gateway for further functionalization, it destroys the electrical conductivity of carbon nanotubes by making them insulators with a resistance of >20MΩ as opposed 10-15Ω of un-functionalized nanotubes[8]. According to one scheme [9], fluorinated nanotubes can be prepared by first oxidizing pristine nanotubes with nitric acid. This removes the catalytic particle at the tip and introduces carboxylic acid residues instead. Cleaned nanotubes are then placed in a furnace and under a combined fluorine and nitrogen gas rate of 30 sccm where they are fluorinated for ten hours. Recently, Gu and co-workers have demonstrated that fluorinated nanotubes can be cut into smaller pieces through pyrolysis [10]. Using a scheme similar to the one discussed above, fluorinated carbon nanotubes were produced that had a stoichiometry of CF_x, where $x \leq 0.2$. Following growth, the nanotubes were put in the furnace of gravometric analysis and pyrolyzed in an Argon atmosphere to 1000°C. Although the exact mechanism is not clear, researchers think that fluorine forms well define, localized bands orthogonal to the nanotube axis. Pyrolysis cleaves the fluorinated part, leaving the

unfunctionalized shortened tubes behind.

- **Free Radical Reaction**

Yunming et al. functionalized SWNT sidewalls using organic radicals that were generated

following decomposition of benzoyl peroxide in the presence of alkyl iodides [11]. As Figure 3 shows, thermal energy started the radical reaction by creating phenyl radicals. These radicals reacted with alkyliodides, which generated iodobenzene and alkyl radicals. Using this procedure, the researchers were able to attach long chain alkanes, alkyl halides, amides, nitriles and ethers to the sidewalls of the carbon nanotubes. Like fluorination, this reaction also destroyed the de-localized π electron network, rendering the nanotube non-conductive.
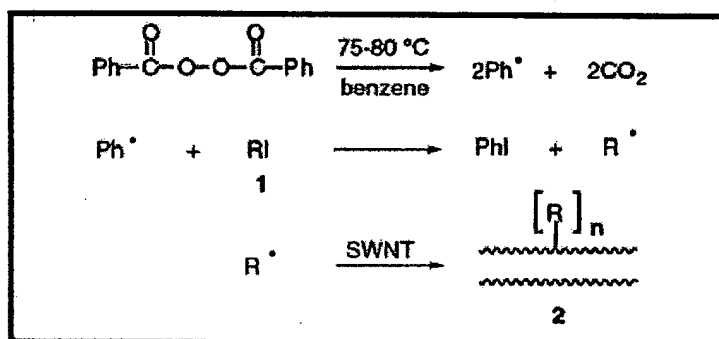

Figure 3: Scheme 1 used benzoyl peroxides as the radical source coupled with alkyl halides to generate alkyl radicals. [Taken from Org. Lett 5(9) 1471].

The researchers also used Minisci method of generating methyl radicals. These radicals although bonded to the sidewalls, but the resulting nanotubes were generally not soluble in most organic solvents[11]. The essential feature of this scheme is the use of iron catalyst in the presence of peroxide. This generates hydroxy radicals, which react with sulfoxides to generated methyl radicals. Results from Scheme 1 and Minisci's method were confirmed using Raman and IR spectra.

- **Solubilization with Polymer**

Chen et al. report solubilization of small diameter nanotubes using rigid side chain poly

(aryleneethynylene) (PPE) polymer [12]. They dissolved SWNT in methylene chloride by mixing 1 or 2 along with vigorous stirring or sonication. This yielded a solubility of 2.2mg/mL, the highest yet reported for a non-covalently functionalized nanotube. Reserachers believe that the most probable mechanism is a π stacking which stabilizes the polymer-nanotube interaction. In addition, this approach

allows covalent modification with neutral and ionic species along the nanotube sidewall.

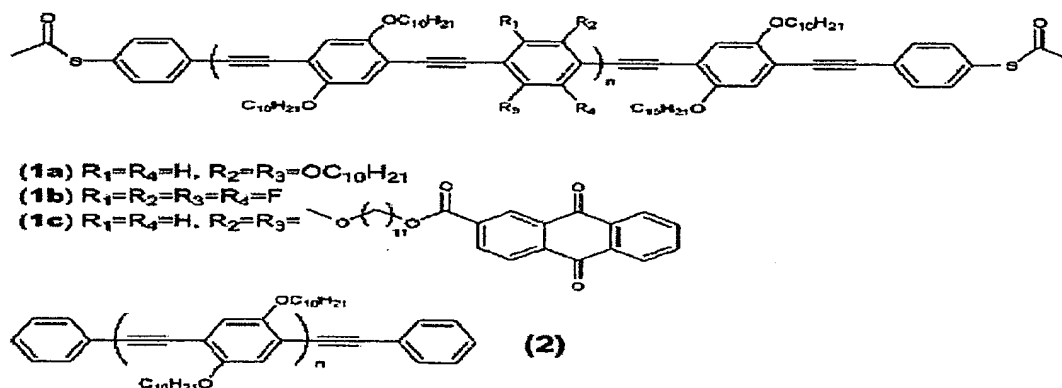Solubility and possibility of modification make this an especially useful procedure.

(1a) $R_1=R_4=H$, $R_2=R_3=OC_{10}H_{21}$
(1b) $R_1=R_2=R_3=R_4=F$
(1c) $R_1=R_4=H$, $R_2=R_3=$

Figure 4: PPE with side chains[*Taken from* J. Am. Chem. Soc.; 124 9034]

- **Solvent Free Modification**

Although effective, the above mentioned functionalization reactions require a lot of solvent, on

average 2L purifying solvent per gram of nanotube. Dyke et al have developed a mechanism that

circumvents the need for copious amounts of solvent[13]. They used 4 equiv/(mol carbon) of aniline

and SWNT. To the mixture, they introduced Isoamyl Nitrate. The resulting paste was vigorously stirred

and then thoroughly washed and filtered. The resulting nanotubes were functionalized with various

halobenzenes and phenyl groups. This method could potentially be scaled up for large-scale

functionalization of carbon nanotubes.

- **Attaching Metallic groups on Sidewalls**

Coleman et al. report using Bingel reaction, which is a [2+1] cycloaddition to attach gold

colloids to the sidewalls[14]. The reaction entailed reacting diethyl bormomalanoate and 1,8-

diazobicyclo[5.4.0.]undecene (DBU) with pristine single wall carbon nanotubes. Following filtration

and thorough washing cycles, the $(COOEt)_2$—SWNT underwent transesterification with 2-(methylthio)

ethanol. The product of this reaction was thoroughly washed with diethyl ether and then Au colloids

were introduced. The gold colloids tightly bonded with the sulfur atoms of 2-(methylthio) groups.

Atomic Force Microscope was used to image the gold-coated nanotubes, which had well defined gold

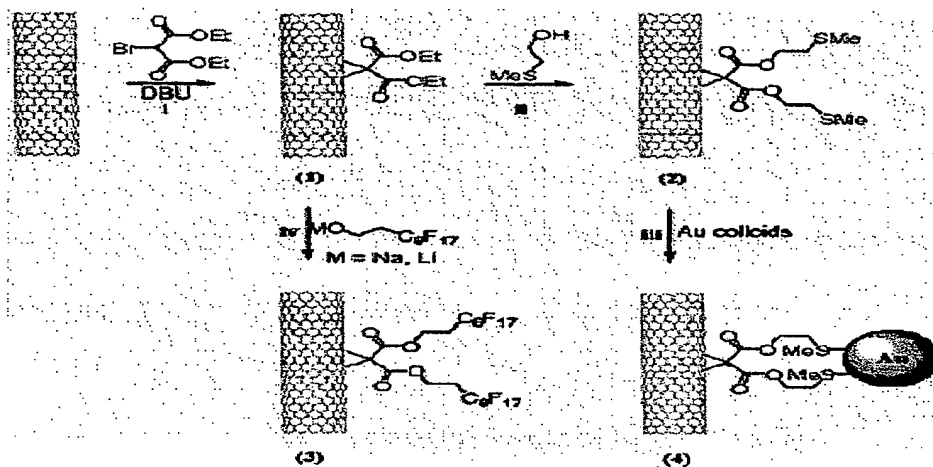colloids on the nanotube, while the perfluordecan-1-ol control nanotubes did not have any.

Figure 5: (i) addition of ethyl bromomalanoate. (ii) addition of 2-(methylthio) ethanol. (iii) introduction of Au colloids (iv) transesterification with perfluordecan-1-ol as a control. [Taken from J. Am. Chem. Soc. 125, 8722.]

Selectivity

- **Differentiation through Modification**

A major hurdle in nanotube chemistry is that most preparatory methods yield a mixture of metallic, semi-conducting, or semi-metallic nanotubes.[15] Strano et al. demonstrated selective chemical functionalization depending on the electronic structure of the nanotube[8]. 4-chlorobenzenediazonium-tetrafluoroborate, a diazonium salt, formed covalent aryl bonds with metallic and semi-metallic nanotubes because they have electrons with energy near the energy of the nanotube's Fermi level. This bond formation destabilized neighboring carbon atoms and made them susceptible to a covalent aryl bond formation. Exploiting this method, nanotubes were reacted to the exclusion of semiconducting nanotubes, which provides a simple and effective selection method. The reaction was monitored using (UV-vis-nIR) absorption spectra, which monitors valence band to conduction band electronic transitions. Following multiple rounds of reaction, the maxima that corresponded to a metallic nanotube's electronic transitions decreased while semiconducting nanotube's peaks (830-1600nm and 600-800nm) remained the same. (See Figure 6 for details).
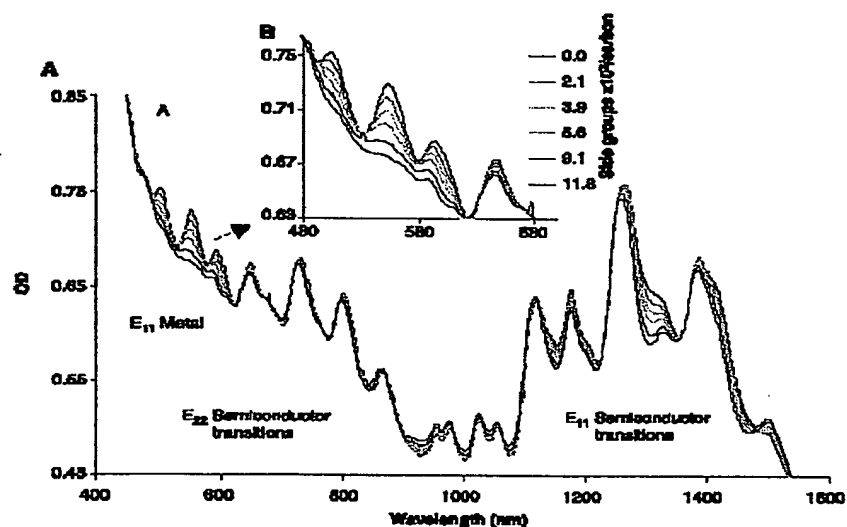
Figure 6: Metallic nanotubes usually absorb in 480-580 range. Inspection of inset shows a decrease in absorption following multiple rounds of reaction. The semiconducting nanotubes, on the other hand, are unaffected. [Taken from Science 301, 1519.]

- **Tunable Differentiation**

[16]

Zhao et al. oxidized carbon nanotubes with 9:1 H_2SO_4/H_2O_2 solution   . This introduced carboxylates at the ends of the nanotube. The nanotubes were purified and suspended in buffers of varying pHs. Results showed that the nanotubes remained water soluble and stable in pH>3 for months, but formed colloids in pH<3. Optical studies done (see Figure 7) on the different pH samples showed that the S_{11} transition decreased with decreasing pH, while the maxima corresponding to metallic nantube transition remained constant. Researchers think that presence of free carboxylic acid groups at the tips of these oxidized tubes has something to do with formation of colloids below pH 3.
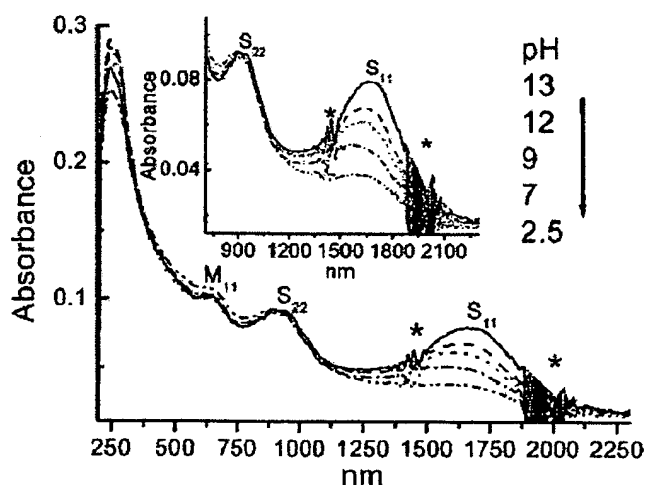

Figure 7: Spectrum shows decrease in absorption in semi-conducting region. Interstingly, the change is reversible, which provides a tunable control of nanotube properties and selection. [Taken from *J. Amer. Chem. Soc.* 124(42),

12418, 2002]

Biological molecules & Applications

- **Nucleic Acid Attachment**

Nguyen et al. functionalized Multi-Wall Carbon Nano-Tubes (MWNT) with nucleic by oxidizing

the nanotubes and using a spin on glass coating on the surface of the nanotubes to keep the nanotubes

firm and vertical [17]. Using water soluble coupling reagents 1-ethyl-3(3diethylaminopropyl)

carbodiimide hydrochloride (EDC) and N-hydroxysuflo-succinimide (sulfo-NHS). EDC helped activate

the carboxylic acid groups at the tips of oxidized MWNT and made o-acylisourea intermediate. This

intermediate undergoes hydrolysis with sulfo-NHS to make a succinimidyl intermediate. Subsequently,

the tubes reacted with primary amine on an oligonucleotide to make amide linkage. Finally, the nucleic

acid solution was added. The researchers used fluorescent microarray and Cy3 DNA label to detect

presence of nucleotide on nanotube surface. Their results show that spin on glass is an essential

component for their reaction because without this support, nanotubes collapse and are an inefficient
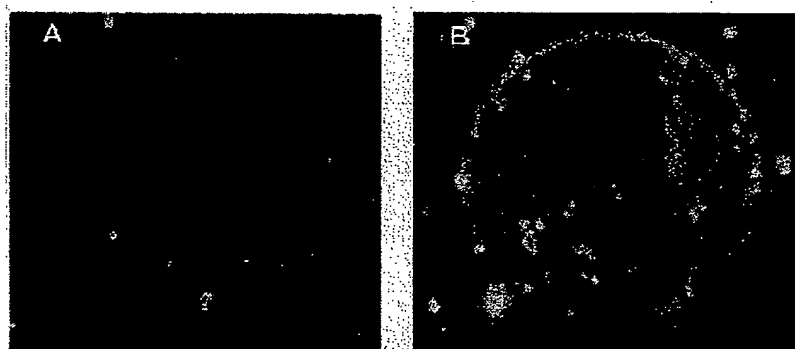
substrate.

Figure 8: (A) CNT without SOG (B) CNT with SOG[Taken from *Nano Letts. 2(10), 1079-8, 1079-81]*

- **Controlling Protein Modification**

Shim et al. produced a method for controlling nonspecific protein adsorption to nanotubes [18].
The researchers used Triton X-100 or Triton X-405 as a wetting agent to coat the surface. This surface

was subsequently dipped in a polyethylene glycol (PEG) which homogenously coated the entire surface

of the tube. This coating prevented the binding of streptavidin which otherwise readily binds with single

wall nanotube through non-covalent pi-pi interaction. In addition, all other proteins were also repelled.

Next, the researchers exploited streptavidin-biotin affinity to specifically bind streptavidin to biotin ligands without having the protein adsorb to the surface of the nanotube. The results were confirmed with Atomic Force Microscope images. Such control in protein modification holds significance for further work in protein resistance and antibody-antigen binding using nantoube biosensors.

Device Application

Krupke et al. have demonstrated that a single nanotube bundle can be aligned using alternating electric field [19]. They used Ag-Au electrodes because they stronger interaction with the carboxylic groups at the tips of carbon nanotubes. First, they made a mask and setup an oscillating electric field using a low-impedance frequency generator. Then they put a drop of nanotube solution on the chip. After few minutes, they dried off the drop and imaged to see that the nanotube bundle was extremely well aligned (see Figure 8). The optimum frequency for alignment was 1 khz. This result is a remarkable improvement for nano-device manufacturing because it gives more control in making complex devices.
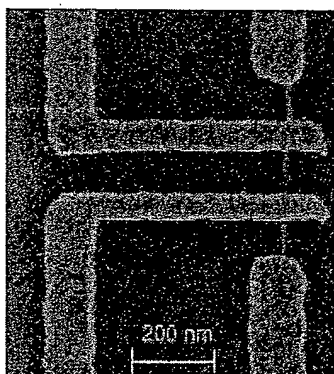

Figure 8: Image of an aligned nanotube that traverses from one electrode to the other. [Taken from *Appl. Phys. A.* 76, 397-400, 2003]

Conclusion

Nanotube functionalization is a field of active investigation with innovations every week. Fluorination has opened nanotubes to a host of new organic synthesis reactions. Solvent-free method allows functionalization without a great deal of solvent for purification, which makes this procedure quite useful for large-scale industrial processes. Work of Strano et al. addresses another major issue in nanotube research by allowing accurate identification and semi-conducting and metallic nantoubes. Nanotube Biotechnology is a rapidly growing field and protein modification is going to be a crucial

element in the development of biological sensors. Finally, nanotube alignment is a necessity for integrated circuit design because there is very little room for 'deviations' in chip fabrication. For this reason, Krupke's study could prove immensely useful in aligning nanotubes between electrodes.

Although these findings are significant, a lot of work still remains to be done. First, nanotubes must be well purified so as to completely separate metallic and semi-conducting nantoubes. Secondly, new ways of non-covalent modification should be developed that would allow the nanotube to be temporarily or permanently functionalized for specific operations. Nanotubes are still far from making the impact that they should be making in biological research. Towards that end, nanotubes should be made that can traverse cell membrane and not kill the cell so that they could become sensors for proton gradient and more.

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